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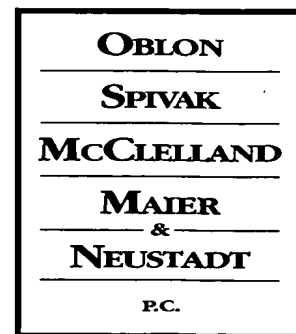
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Docket No.: 245926US0X DIV

COMMISSIONER FOR PATENTS  
ALEXANDRIA, VIRGINIA 22313



ATTORNEYS AT LAW

RE: Application Serial No.: 10/720,122  
Applicants: Toshio TSUJIMOTO, et al.  
Filing Date: November 25, 2003  
For: SURFACE MODIFICATION PROCESS OF QUARTZ  
GLASS CRUCIBLE  
Group Art Unit:  
Examiner:

SIR:

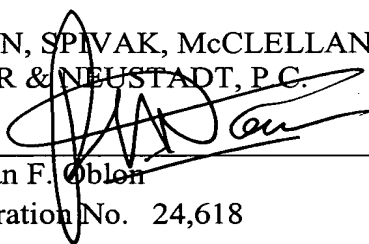
Attached hereto for filing are the following papers:

**Preliminary Amendment; Request for Priority; Priority Document (1); Attachments (3)**

Our check in the amount of \$0.00 is attached covering any required fees. In the event any variance exists between the amount enclosed and the Patent Office charges for filing the above-noted documents, including any fees required under 37 C.F.R. 1.136 for any necessary Extension of Time to make the filing of the attached documents timely, please charge or credit the difference to our Deposit Account No. 15-0030. Further, if these papers are not considered timely filed, then a petition is hereby made under 37 C.F.R. 1.136 for the necessary extension of time. A duplicate copy of this sheet is enclosed.

Respectfully submitted,

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## 第2項 CZ法 (CZ Pulling)

About 85 % of all semiconductor devices are made from Czochralski (CZ) grown silicon single crystals. The main reason for this frequent usage of CZ silicon is its oxygen content which involves two beneficial effects in device manufacturing: hardening and internal gettering. Of only second importance is the circumstance that CZ silicon crystals can be easier grown to large diameters than float-zone silicon. At present, the main development goals for CZ-Si growth are the growth of 200 and 300 mm diameter crystals with higher dislocation-free yield, higher purity in respect to harmful fast diffusing elements like copper and nickel, and reduction of the self-point defect related microdefects, e.g. "D-defects", which especially injure the thin gate oxides. The classical CZ-Si growth process is no more able to produce large crystals from melts of 100 kg or even 300 kg with sufficient yield and quality. Therefore, special means like heat shields and magnetic fields must be used to reduce the temperatures, the fluctuations in temperature and the oxygen content of the melt and to control the oxygen supply to the crystal. The CZ-Si crystals have, compared to float-zone silicon, a long thermal history which gives rise to additional axially varying crystal properties. Therefore, special care must be taken to control the thermal history and its effects on crystal quality.

### 1. Introduction

More than 98 % of all electronic devices are made from single crystalline silicon. Two methods are applied in the industry for the growth of silicon single crystals: The Czochralski (CZ) growth method, which yields more than 85 % of all silicon single crystals, and the float zone (FZ) growth method, which yields the rest. CZ-Si crystals are mainly used for the manufacturing of highly integrated low power devices, typically for microprocessors, RAMs, DRAMs, ASICs, etc., whereas FZ-Si crystals are mainly used for the manufacturing of discrete or low integrated high power devices, typically for diodes, transistors, thyristors, etc. The high oxygen content of the CZ-Si crystals (typically 14 ppma in 1995) is the reason for its use in the manufacturing of highly integrated devices. Oxygen reduces the formation and mobility of dislocations in silicon during the high temperature device processes and, additionally, generates an internal gettering effect which prevents the precipitation of fast diffusing impurities like copper or nickel in the vulnerable electronic structures at the wafer surface. In contrast, the oxygen content of FZ-Si is very low, typically 0.04 ppma, i.e. too low for hardening and internal gettering. In 1994, the new and largest standard CZ-Si crystal diameter in industry was set to 300 mm. In experiments, CZ crystals of up to 400 mm in diameter have been grown till 1995.

tain the highest density of homogeneous precipitation nuclei.

The behavior of the vacancies and self-interstitials during cooling is more complex and not completely understood till today, but is of comparable technical importance as the oxygen precipitation<sup>21) -23)</sup>. The self-point defects can influence many properties of a crystal. For example, vacancies seem to be responsible for the formation of the flow-pattern defects (named after their etch figure), also called "D-defects". It is not probable, that they are real D-defects (pure and small agglomerates of vacancies), because they create relative large etch pits with evolution of gas.

## 10. Large diameter crystals

The main problem of the growth of large diameter silicon crystals is, that the yield of dislocation-free crystals decreases continually with increasing crystal diameter. Decreasing dislocation-free yield increases the costs per kilogramm of dislocation-free crystal or square centimeter of a polished wafer, respectively.

There are some basical physical factors which obstruct the economical production of silicon crystals of large diameters:

The ratio between crystal length and crystal diameter, the volume of the CZ-Si melt, the cooling strains in the crystal<sup>29)</sup>, the time for melting and growth of the crystal, and the temperatur at the crucible wall. These effects have a strong impact on the dislocation-free yield of the growth process and are therefore of great economical importance.

### 10.1 Ratio between diameter and length

The most simple basic factor is the ratio between crystal length and crystal diameter, which determines the yield loss resulting from the running back of dislocations into the dislocation free crystal when dislocations occur at the growth interface. If some dislocations are generated by a disturbance at the growth interface of a larger d is location-free silicon crystal, then the dislocations, driven by the

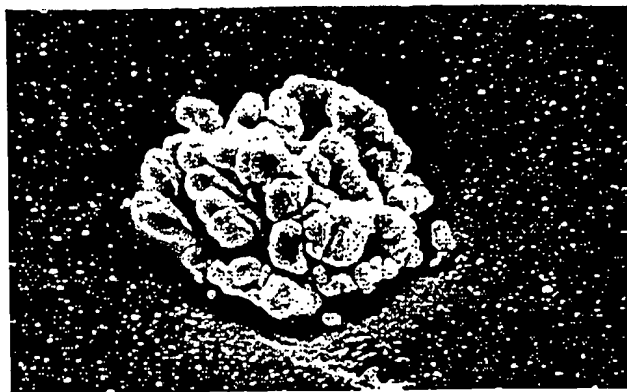


Photo.2 Cristobalite micro crystal ( $\approx 10\mu\text{m}$  diameter) on a silica sample generated and grown after 5 min of immersing the silica sample into a CZ-Si melt at  $1460^\circ\text{C}$  and 15mbar (12 mbar argon + 3 mbar liquid silicon); scanning electron microscopic (SEM) picture.

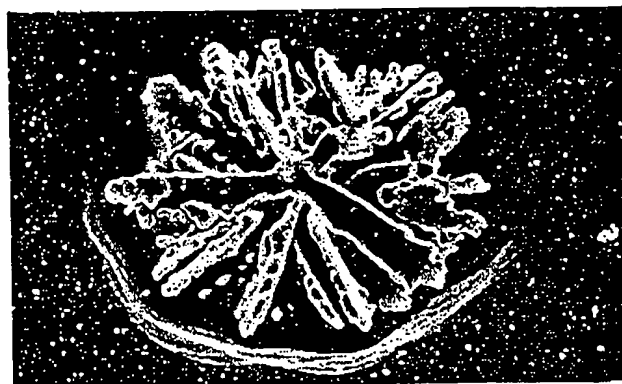
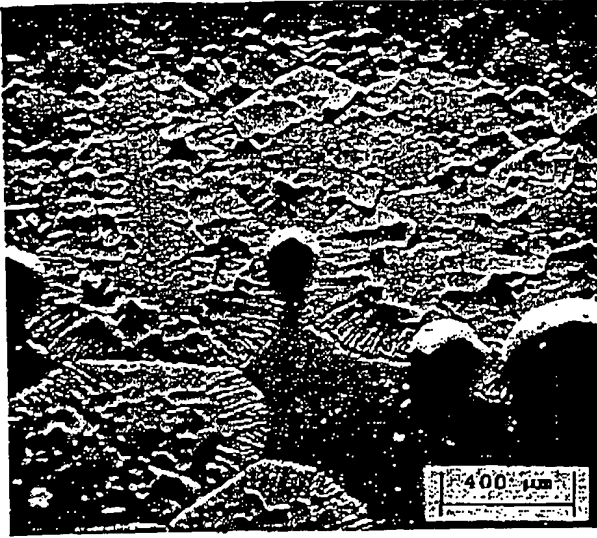
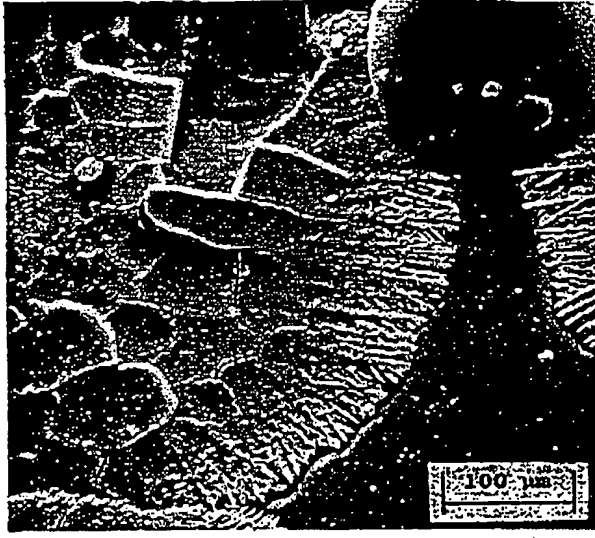


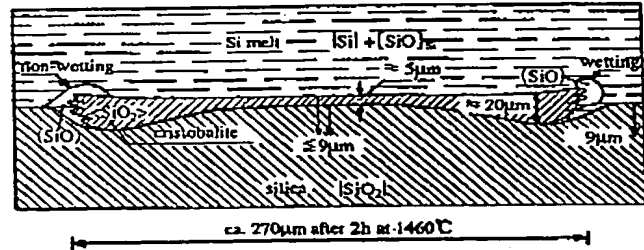
Photo.3 Cristobalite crystal rosette ( $\approx 90\mu\text{m}$  diameter) on a silica sample generated and grown after 40 min of immersing the silica sample into a CZ-Si melt at  $1460^\circ\text{C}$  and 15mbar. A silicon melt droplet (now frozen) remained sticking between the cristobalited-endrites and the silica at a site where the melt was in the wetting state during pulling out of the silica sample from the melt; SEM picture.



**Photo.4** Circular cristobalite layers ( $\approx 675\mu\text{m}$  diameter) on a silica sample generated and grown after 5 h of immersing the silica sample into a CZ-Si melt at  $1460^\circ\text{C}$  and 15mbar (12 mbar argon + 3 mbar liquid silicon). Silicon melt droplets (now frozen) remained sticking at the dendritic rim of cristobalite layers sites where the melt was in the wetting state during pulling out of the silica sample from the melt. The cristobalite layers are cracked during cooling owing to transformation from  $\beta$ -cristobalite into  $\alpha$ -cristobalite at  $275^\circ\text{C}$  and show no pitting corrosion. The smooth and not cracked surface is silica; SEM picture.



**Photo.5** Enlarged detail of Figure 12 showing the dendritic rim and a sticking frozen melt droplet; SEM picture.



**Fig.9** Vertical section through a circular cristobalite layer drawn in correct proportions according to microscopical observations. The layer grows only in radial direction and is built up, in principle, from the silica which has been removed from the surrounding ditch by the wetting/non-wetting process at the three phase boundary silica/melt/SiO-gas. Most time, the dendritic rim is covered by a SiO gas bubble. At  $1460^\circ\text{C}$  and 15 mbar, the layer grows with a constant thickness of ca.  $20\mu\text{m}$  at the dendritic rim. The layer thickness decreases toward the center of the layer owing to dissolution by the melt and remains nearly constant at ca.  $5\mu\text{m}$  thickness in the center. This constant thickness leads to the conclusion that the cristobalite layer spreads also into the silica by devitrification.

cooling strains, very rapidly multiply and spread over the whole cross section of the crystal and back into the formerly dislocation-free crystal as far as one diameter away from the growth interface. The crystal further grows dislocated, and with large diameters, the dislocated growth changes soon to polycrystalline growth.

Owing to the back running of dislocations, the dislocation-free yield of large diameter crystals is strongly impaired by their disadvantageous ratio between crystal diameter and crystal length. For

example, a crystal of 30 cm diameter has a cylindrical length of ca. 70 cm if it is pulled from a melt of 150 kg Si. A big part of the melt is consumed by the seed and end cones and by the residual melt. For such a 30cm diameter crystal, the ratio of diameter to length is  $30/70 = 0.43$ , i.e. ca. 43 % of the formerly dislocation-free crystal is deteriorated, when dislocations occur at the cylindrical end of the crystal body (what often happens because of the difficulties with the end conegrowth of 30 cm diameter crystals). The relative loss increases rapidly with decreasing length and reaches 100 % at a cylindrical length of ca. 30 cm, i.e. if the crystal gets dislocations at about the half of its maximum length than the total crystal is useless.

This yield loss problem is much smaller with crystals of smaller diameters. For example, a crystal of 10 cm diameter and 180 cm (typical) length has a ratio of diameter to length of  $10/180 = 0.056$ , i.e. only 5.6 % of the crystal is deteriorated when dislocations occur at the end of the cylindrical crystal body.

## 10.2 Temperature fluctuations

As shown in the chapter "Melt flows", the thermal convection increases with the third power of the melt height and linearly with the temperature difference in the melt. This means that with very large melts, the melt flows become very turbulent and chaotic, what results in larger temperature fluctuations at the growth interface, in particular at its susceptible edge. On the other hand, the cooling strains in the crystals increase continually with increasing diameter and come closer to the yield strength of the crystal, at which first dislocations are generated in a dislocation-free crystal<sup>29)</sup>.

Temperature fluctuations generate fluctuating additional strain in the crystal. In particular at the beginning of growth, when the melt is heighest, the

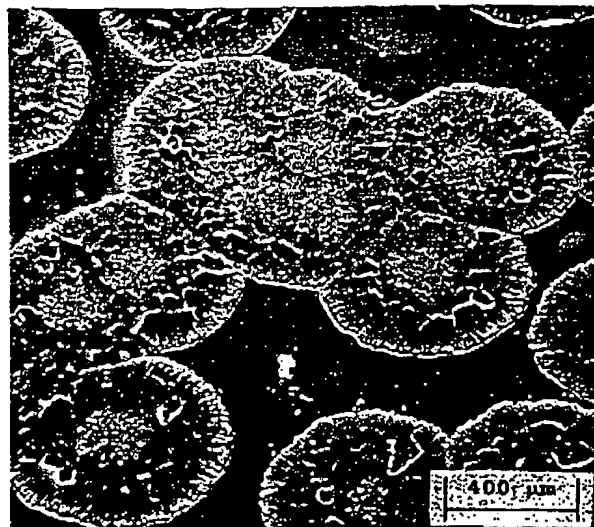


Photo.6 Pitting corrosion in the center of circular cristobalite layers on a silica sample after 5 h of immersing the silica sample (different from that of Figures 12 and 13) into a CZ-Si melt at 1460 °C and 15 mbar. The cristobalite layers are cracked owing to transformation from  $\beta$ -cristobalite into  $\alpha$ -cristobalite at 275 °C; SEM picture.

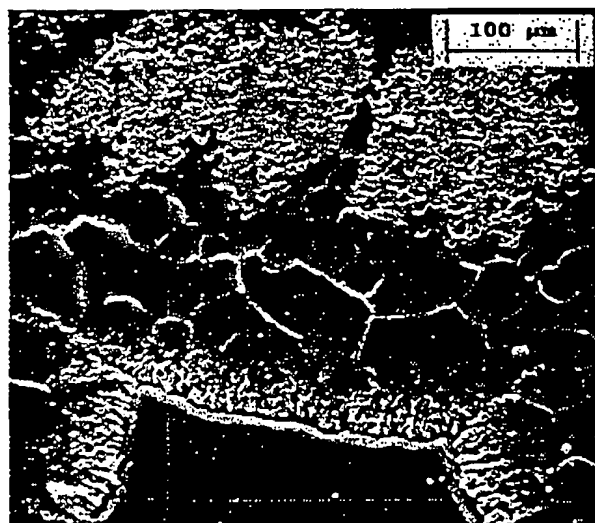


Photo.7 Enlarged detail of Figure 15 showing pits in the cracked cristobalite layer, dendritic rim and smooth silica surface; SEM picture.